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Study of Beta – irradiation effects on polymethylmethacrylate (PMMA) using (PALT), low doses

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Abstract Beta low dose-irradiation effect on polymethylmethacrylate (PMMA) samples has been investigated for the first time with the use of Positron Annihilation Lifetime Technique (PALT). The orthopositronium (o-Ps) lifetime τ_3, component, hence its parameters, the free-volume hole size (V_h), the free volume fraction (f_h) and the free positron annihilation lifetime τ_2 were measured and studied as a function of Beta dose up to 30.28 kGy.

It has been shown that τ_3, V_h and f_h increase with increasing Beta-dose, to reach a maximum percentage increment of 19.1%, 33.3% and 61.1% respectively at 0.075 kGy, whereas τ_2 reaches the maximum percentage changes of 73.7% at 3.1 kGy. Beyond those doses the values fluctuate up to a maximum Beta-dose of 30.28 kGy. The results suggest that Beta-irradiation induces structure damage in PMMA, causing degradation in the main chains, whereas the presence of oxygen (irradiation in air) causes reduction in the amorphous volume creating a net reduction of the degradation yield, which consequently affecting the values of the above mentioned parameters with respect to their values in case the irradiation is performed in vacuum.

Keywords Beta irradiation, PMMA, positron lifetime

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1 Introduction

Positron annihilation spectroscopy (PAS) has been recently developed to determine the defect properties at the atomic level for polymer materials (1). The sensitivity of PAS is due to the localization of positronium (Ps) in those holes range from 1Å to 10 Å. Positron annihilation spectroscopy has emerged as a unique and potent probe for characterizing the free – volume properties of polymers (2).

In PAS one employed the antiparticle of electron, th positron as a nuclear probe. Because of its positively charged nature, the positron is repelled by the ion cores and preferentially localized in the atomic – size free-volume holes (V_h) of a polymeric material. Therefore, the positron and positronium (a bound atom which consists of a positron and an electron) annihilation signals are found to be contributed mainly from the free-volume holes in a polymer. Currently, PAS has been mainly developed in monitoring the ortho-Positronium (o-Ps), a triplet state, annihilation lifetime (PAL) for polymeric applications. The results for (o-Ps) lifetime and its probability are related to free-volume hole size, fraction and distribution. Experimental (3, 4) and theoretical efforts (5-7) suggested that PAL is a unique probe which can directly measure the free-volume hole size in amorphous polymers.

The results for o-Ps lifetime and its probability, are related to free-volume hold radius R (8) as :

$$\tau_{o\text{-}Ps} = 0.5\left[1 - \frac{R}{Ro} + 0.159 \sin\frac{2\pi R}{Ro}\right]^{-1} ns, \qquad (1)$$

where $R = Ro + \Delta R$ and $\Delta R = 0.1656$ nm, the electron layer thickness.

The free volume fraction (f_h) can be expressed as an empirical eq. (9).

$$f_h = AV_h I_3 , \qquad (2)$$

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where V_h (in nm^3) is the free – volume hole size to be calculated, using the spherical radius (R) from eq (1), τ_3 (in ps) is the lifetime, I_3 (in %) is the intensity, and A is a constant, which is empirically determined to be (1-2) (nm^{-1}) in solid polymers

PMMA is an amorphous polymer that usually suffers from degradation in the side chain (scission) by irradiation. One important result of this effect is its molecular weight reduction. The number of molecules per unit mass is proportional to the reciprocal of molecular weight (10, 11). It was found that 60-65 eV deposited energy (of ^{60}Co γ-ray) causes one scission in PMMA (12) at room temperture. If the reciprocal of the polymer molecular weight is plotted against the absorbed dose, there must be a linear relation (a straight line) of a positive slope proportional to the radiation energy absorbed per unit scission in the polymer chain (10, 13).

Ito and Tabata (14) reported the polymerization of the (PMMA) methylmethacrylate monomer using γ-rays irradiation by means of PALS. They found that both τ_3 and I_4 were increasing with increasing the absorbed dose up to MGy

Al-Bayati and Coworker (15, 16) investigated γ-irradiation efects on PMMA using PALS. They concluded that a reduction of the amorphous regions of PMMA occurred as the dose increased up to 880 KGy. The reduction of the lifetime indicated that free volume size reduction and therefore the expected effects are due to the cross-linking, due to the oxygen presence and the interactions with the peroxy radicals at reactive sites of PMMA Rubilio *et al* (17) have investigated the effects of γ-irradiation on PMMA with a total dose of 200 kGy using PALS, as well as the mechanical properties of that polymer. The free volume content of non irradiated and the irradiated polymers clearly demonstrated increment as the dose increased. They explained the results due to the scission and the rapture of the polymer chains.

2. Experimental and data analysis

The PMMA samples were prepared in the laboratory, with a diameter of 32 mm and thickness of 1.5 mm.

The samples were irradiated in air at room temperture by Beta – irradiation using a $^{90}Sr/^{90}Y$ source of 1 Ci activity ($E_{(\beta)max}$ = 2.28 MeV). The dose rate was 0.302 kGy / h The irradiation was performed up to a total dose of 30.28 kGy The

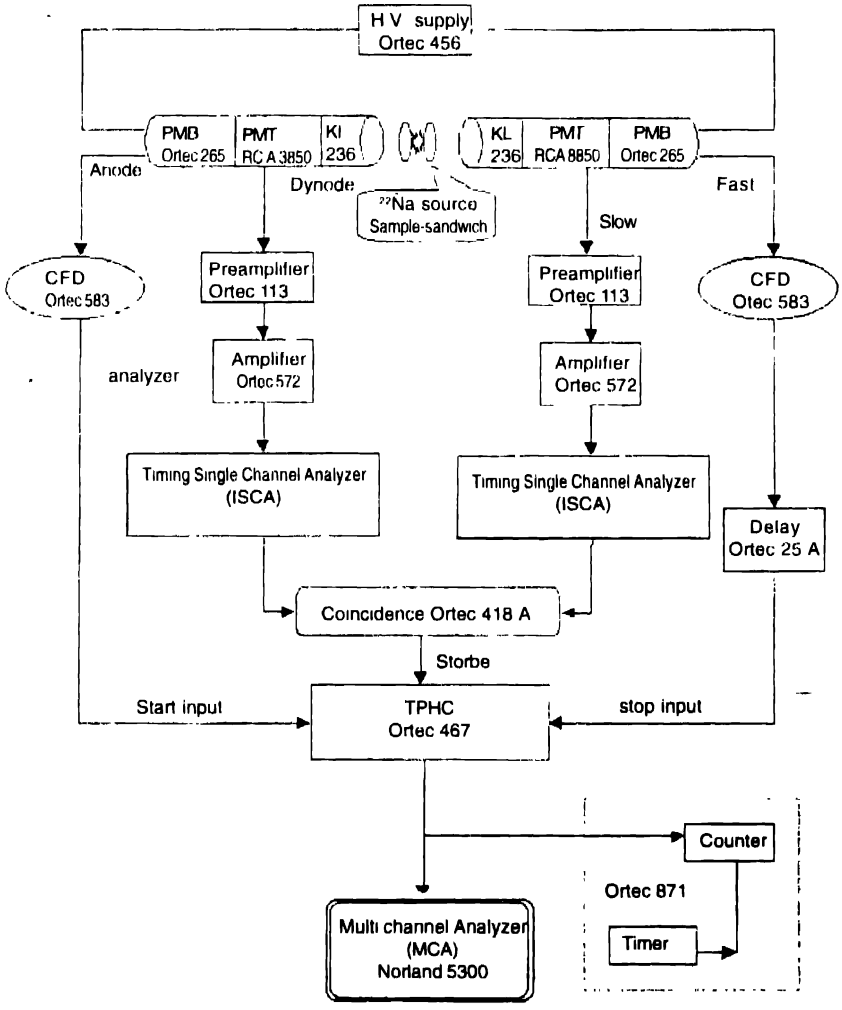

Figure A. A block diagram of the experiment setup.

positron lifetime measurements were performed using a fast-slow coincidence system (15) Figure A, with a time resolution of 400 ps. The positron source activity was 2.14 uci ^{22}Na and the fraction of positrons absorbed in the source was found to be 8% and corrected for it. Also a background radiation was corrected for.

The lifetime spectra were measured for each individual dose value with a total integral counts of 0.5×10^6. The peak -to-back ground ratio was better than 2200 : 1. The lifetime spectra were analyzed in three-lifetime components using PFPOSFIT program (18). The lifetime components, their relative intensities and the parameters of the prompt curve, were simultaneously fitted The free-volume hole size (V_h) and the free volume fraction (f_h), were calculated using eqs. (1) and (2), respectively.

The corresponding changes in V_h and f_h are 39.6% and 37.3%, respectively. As β^- -dose increases. τ_3 decreases to 2147 ps

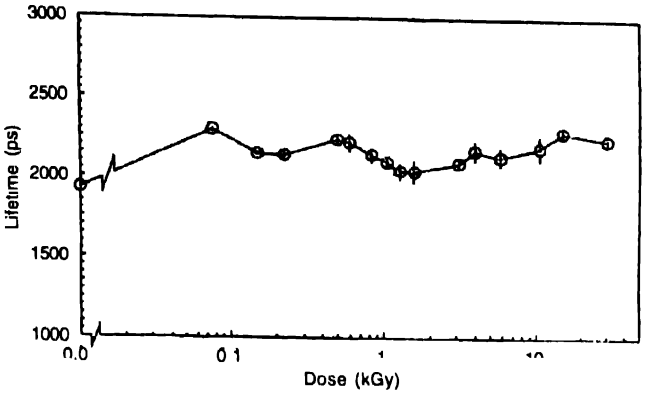

Figure 1(a). Beta-ray irradiation effects on lifetime τ_3 in PMMA

Table 1. The lifetime parameters of β^- -irradiated PMMA (τ_1 fixed at 172 ps)

Dose (kGy)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	V_h (nm^3)	f_h (%)
0	438 ± 21	65 24 ± 1 70	1925 ± 24	8 14 ± 0 21	0 0906	1 106
0.075	678 ± 61	42 40 ± 2.40	2296 ± 29	8.02 ± 0 10	0 1262	1.519
0.151	560 ± 72	24.30 ± 4.40	2147 ± 30	8 00 ± 0 20	0.1115	1 338
0 227	503 ± 22	16.70 ± 0 90	2138 ± 36	7 92 ± 0 28	0 1106	1 314
0 504	617 ± 81	11.30 ± 3 20	2239 ± 35	7 84 ± 0 04	0 1206	1 418
0 604	682 ± 96	17.18 ± 1 50	2219 ± 55	7 93 ± 0 41	0 1136	1 412
0.768	589 ± 22	18 10 ± 2 20	1878 ± 69	750 ± 0 14	0.0862	0.969
0 840	590 ± 80	16.90 ± 1 40	2140 ± 46	7 88 ± 0 30	0 1108	1 227
1 060	582 ± 24	15 40 ± 1 40	2096 ± 34	7 02 ± 0 40	0 1066	1 122
1.284	625 ± 101	9.80 ± 2 80	2041 ± 48	7 40 ± 0 50	0 1013	1 125
1 590	738 ± 110	8 40 ± 1 70	2037 ± 64	6 48 ± 0 87	0 1009	1 051
3 100	761 ± 128	8 60 ± 0 90	2085 ± 80	6 62 ± 0 17	0 1055	1.048
4 000	727 ± 93	8 08 ± 1.80	2166 ± 68	6.49 ± 0 61	0 1140	1 104
5 820	643 ± 81	7.70 ± 1 56	2126 ± 55	6 51 ± 0 22	0 1095	1 069
10.650	689 ± 12	8 12 ± 0 30	2184 ± 72	6 53 ± 0 40	0 1151	1 262
15 180	536 ± 24	7 46 ± 1 60	2281 ± 31	6 64 ± 0 21	0 1247	1 242
30.280	501 ± 12	7.82 ± 0 93	2235 ± 25	6 50 ± 0 43	0 1202	1 175

3. Results and discussion

The results of the analysis of β^- -Irradiated PMMA lifetime spectra are listed in Table 1. Figures 1(a) and 1(b) represent the o-Ps lifetime and the corresponding intensity, whereas Figures 2(a) and 2(b) show τ_2 and I_2 as a function of the absorbed dose, respectively. In Figures 3(a) and 3(b), the values of V_h and f_h are plotted *versus* β^- -doses, respectively.

From Table 1, it is shown that the first β^- -dose of 0.075 kGy induces a high change in τ_3, where an increment of 19.2% takes place.

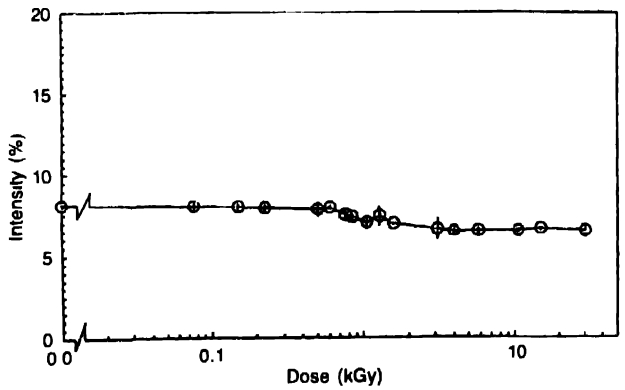

Figure 1(b). Beta-ray irradiation effects on I_3 in PMMA.

and it remains at that value upto β^--dose of 0.504 kGy. At that dose, τ_3 increases about 16.2%, corresponding to 33.2% and 28.29% increments in V_h and f_h, respectively. For the dose range from 1.06 kGy to 3.10 kGy, only small changes of 8% in τ_3 occur, corresponding to 15% and 1% changes in V_h and f_h, respectively. Another increment in τ_3 of 18.49% occurs at β^--dose of 15.18 kGy, corresponding to 37.7% increment in V_h and 12% increment in f_h.

Although the first β^--dose is small, it induces a sharp increment in τ_3, as shown in Figure 1(a). Such a rise could not be explained on the bases of the chain scission only, because of the expected small changes in M_n (19),

$$\text{where } \frac{1}{M_n} = 1.844\times10^{10} D(Gy) + 9.738\times10^{-7} \quad (3)$$

for the values given in Ref. (19)

$$\text{and } \frac{1}{M_n} = 1.5504\times10^{-10} D(Gy) + 3.803\times10^{-7} \quad (4)$$

for the values given in reference (17)

Formulae (3) and (4) are deduced from the formula (20):

$$\tau_3 = \frac{1}{\lambda_0 + \Omega M_n} \quad (5)$$

where M_n is the number-average molecular weight of the polymer, Ω and λ_0 are empirical constants.

Furthermore, applying the formula (21):

$$\tau_3 = \frac{1}{\lambda_3} \quad \frac{1}{\lambda_3 + \Omega M_n + K[X]} \quad (6)$$

where λ_3 is proportional to the o-Ps pick off annihilation rate at $[X] = 0$, $K[X]$ is the chemical effect rate, $[X]$ is the concentration of some chemical species, one can get the contribution of the chemical effect rate K[X] approximately. Table 2 gives the calculated values. In Figure 4 these values are plotted *versus* the absorbed β^--doses.

Also the free radical's contribution in such a small dose is not high enough to induce such a change in τ_3. Therefore such an increment in τ_3 could be due to the sudden rupture of PMMA chain as a result of β^--rays irradiation with a dose of 0.075 kGy. When this happens, there will be cracks, where a high fraction of Ps atoms are trapped in. This causes an increment in the free volume and thus τ_3 increases. From higher β^--doses the changes in τ_3 are as expected due to reducing M_n.

Using formulae (3) and (4), and fitting τ_3 values (Table 1) to the formula (5), the following empirical formulae could be found for β^--dose range from 0 to 0.504 kGy:

$$\tau_3 = \frac{1}{-1.380\times10^{-5} + 4.848\times10^{-10} M_n} \text{-(Ps)}, \quad (7)$$

$$\tau_3 = \frac{1}{2.245\times10^{-4} + 9.911\times10^{-11} M_n} \text{-(Ps)}. \quad (8)$$

The behavior of τ_3 indicates the high free radicals formation probability for the dose range from 0.840 kGy to 3.1 kGy, where τ_3 shows a constant behaviour, as shown in Figure 1(a). From $(k[X])^{-1}$ values given in Table 2 such a phenomenon could be explained. The changes in the $k[X]$ values are very efficient at that dose interval specifically, indicating that the formation and the reactivity of the free radicals are higher in such a way that the reduction in τ_3 due to the o-Ps lifetime quenching (due to the presence of the free radicals) is of the same order of the increment in τ_3 due to the reduction in M_n. At a dose of 5.82 kGy, τ_3 shows some recovery of its high values, such an increment is in an agreement with the changes in $(k[X])^{-1}$ values given in Table 2.

The o-Ps inhibition is very clear from the reduction in I_3 values, as observed in Figure 1(b). The change of I_3 values also

Table 2. $1/k\,[X]$ values as calculated using formulae (6) and (7) and formulae (3) and (4)

Dose (kGy)	τ_3 (ps)	$1/k[X]$ (from eq (6) (ps)	$1/k[X]$ (from eq. (7) (ps)
0 768	1878	9062	9206
0 840	2140	19392	20455
1.060	2096	13109	14114
1 284	2041	9648	10538
4 000	2166	5202	7229
15 180	2281	3089	5622
30 280	2235	2582	4911

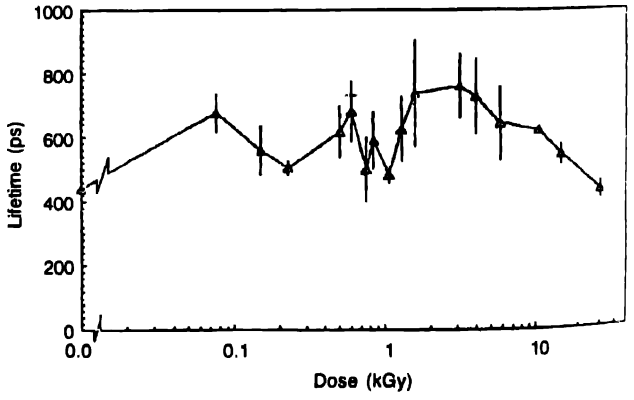

Figure 2(a). Beta-ray irradiation effects on lifetime τ_2 in PMMA

include the effects of the free radicals within the dose range from 0.84 kGy to 4.0 kGy, where the reduction is of a higher rate at such doses. From fitting the values of I_3 to the formula $I_3 = I_{03}e^{-\phi D(Gy)}$, one can find that the values of I_3 taken from Table 2 obey the following empirical formula :

$$I_3 = 8.132\, e^{-9.725\times10^{-5}D(Gy)}. \quad (9)$$

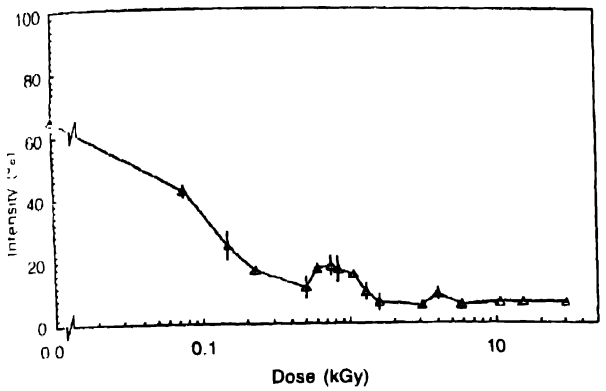

Figure 2(b). Beta-ray irradiation effects on I_3 in PMMA.

Another evidence of the efficient free radicals formation rate is the increasing values of τ_2 as shown in Figure 2(a), where its values increase from 438 ps to 678 ps for the first β^--dose. The threshold Dose (TD) is 3.1 kGy, in this case, τ_2 reaches a maximum of 761 ps, which is 73% higher than the initial τ_2 values (483 ps). The tendency of the sharp decrease in the values of I_2 shown in Figure 2(b) associated with the increment of τ_2, is quite obvious for the β^--dose of 0.075 kGy and 1.284 kGy. This confirms that some transition in the physical system occurs. Such a transition takes place may be beause of the larger lifetime of the free positrons. It is important to point out that irradiation in air is subjecting the irradiated samples to the oxygen which actively reacts with the free radicals created out of the PMMA surface producing a peroxide radicals which cause different polymer structural changes (15) and hence affect the values of τ_3, V_h, f_h. It was found before (15) that in vacuum these parameters have different values, they have larger values in vacuum because in case no air present, no peroxy type radicals there, hence the degradation rate is less in vacuum than in air.

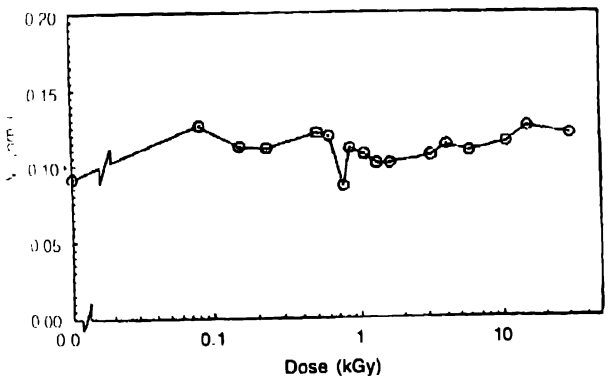

Figure 3(a). Beta-ray irradiation effects on V_h in PMMA

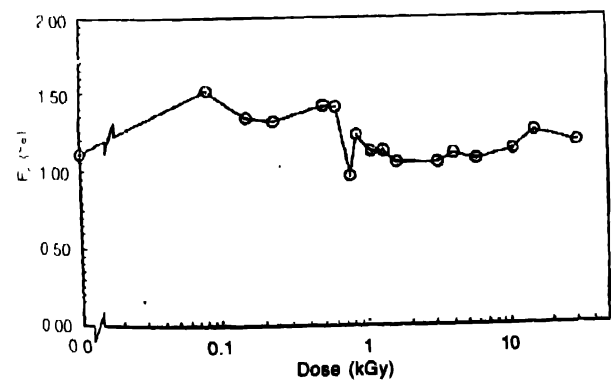

Figure 3(b). Beta-ray irradiation effects on F_h in PMMA

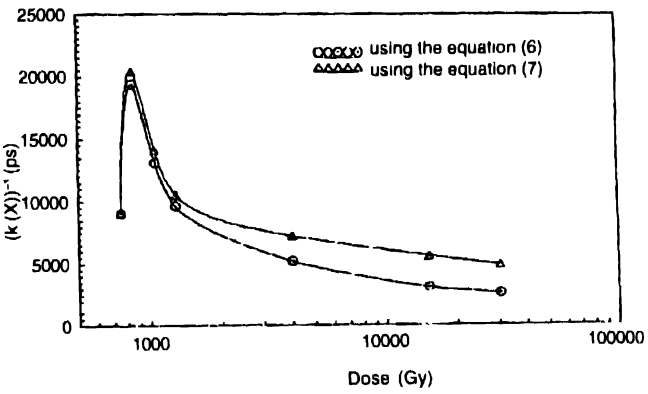

Figure 4. The $(K(X))^{-1}$ values (in ps) for beta-irradiated PMMA *versus* dose

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